

PATENT COOPERATION TREATY

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NOTIFICATION OF ELECTION

(PCT Rule 61.2)

From the INTERNATIONAL BUREAU

To:

Commissioner
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Applicant GIDNER, Anders et al	

1. The designated Office is hereby notified of its election made:

☒ in the demand filed with the International Preliminary Examining Authority on:
 28 March 2001 (28.03.01)

☐ in a notice effecting later election filed with the International Bureau on:

2. The election ☒ was
☐ was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland	Authorized officer Athina Nickitas-Etienne
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INTERNATIONAL PRELIMINARY EXAMINATION REPORT

PCT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference RF 99270PC	FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/SE00/01675	International filing date (day/month/year) 31.08.2000	Priority date (day/month/year) 03.09.1999
International Patent Classification (IPC) or national classification and IPC C02F 1/72, B01J 3/04, B01J 19/00		
Applicant Chematur Engineering AB et al		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.

2. This REPORT consists of a total of 3 sheets, including this cover sheet.

☒ This report is also accompanied by ANNEXES, i.e., sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of 7 sheets.

3. This report contains indications relating to the following items:

- I ☒ Basis of the report
- II ☐ Priority
- III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☐ Certain documents cited
- VII ☐ Certain defects in the international application
- VIII ☐ Certain observations on the international application

Date of submission of the demand 28.03.2001	Date of completion of this report 25.10.2001
Name and mailing address of the IPEA/SE Patent- och registreringsverket Box 5055 S-102 42 STOCKHOLM Facsimile No. 08-667 72 88	Authorized officer Mårten Hulthén/MP Telephone No. 08-782 25 00

I. Basis of the report**1. With regard to the elements of the international application:***

- ☐ the international application as originally filed
- ☐ the description:
pages 1-12, as originally filed
pages _____, filed with the demand
pages _____, filed with the letter of _____
- ☒ the claims:
pages _____, as originally filed
pages _____, as amended (together with any statement) under article 19
pages _____, filed with the demand
pages 13-19, filed with the letter of 03.10.2001
- ☒ the drawings:
pages 1-2, as originally filed
pages _____, filed with the demand
pages _____, filed with the letter of _____
- ☐ the sequence listing part of the description:
pages _____, as originally filed
pages _____, filed with the demand
pages _____, filed with the letter of _____

2. With regard to the language, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language _____ which is:

- ☐ the language of a translation furnished for the purposes of international search (under Rule 23.1(b)).
- ☐ the language of publication of the international application (under Rule 48.3(b)).
- ☐ the language of the translation furnished for the purposes of international preliminary examination (under Rules 55.2 and/or 55.3).

3. With regard to any nucleotide and/or amino acid sequence disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
- ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. ☐ The amendments have resulted in the cancellation of:

- ☐ the description, pages _____
- ☐ the claims, Nos. _____
- ☐ the drawings, sheet/fig _____

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2 (c)).**

* Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are annexed to this report since they do not contain amendments (Rules 70.16 and 70.17).

** Any replacement sheet containing such amendments must be referred to under item I and annexed to this report.

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement**1. Statement**

Novelty (N)	Claims	<u>1-32</u>	YES
	Claims		NO
Inventive step (IS)	Claims	<u>1-32</u>	YES
	Claims		NO
Industrial applicability (IA)	Claims	<u>1-32</u>	YES
	Claims		NO

2. Citations and explanations (Rule 70.7)

Amended claims 1-32 were filed on 3 October 2001.

Document EP 689868 (Page 4, line 35 - line 45; figures 1,5; claims 1, 5-6) discloses a high pressure and a high temperature device for supercritical water oxidation. The device comprises a first conduit adapted to transport a first fluid (oxidant 13) and a second conduit to transport a second fluid (reactant 16). An inner reactor (10) constitutes a part of the second conduit and is made of a temperature and corrosion resistant material.

However, the invention as defined in claims 1 and 15 differs from the above-mentioned device in that it involves a mixing length downstream of the first conduit end equipped with a tube or liner of a corrosion resistant material. The cited document does not reveal that the whole length, which is considered to be equivalent to the "mixing length" according to the invention, is made of a corrosion resistant material. Further, according to the invention, the first conduit ends in the interior of the second conduit.

Other documents cited in the search report are considered less relevant than the above-mentioned document.

The stated differences imply improvements in combating corrosion in a reactor by using the temperature dependence of corrosion, and as a result allowing the main parts of the reactor to be constructed of a relatively inexpensive material. Therefore, the invention as defined in claims 1-32 is considered to involve an inventive step and also to fulfil the criteria of industrial applicability.

CLAIMS

1. In a high pressure and high temperature reaction system suitable for oxidative waste treatment, particularly a reaction system for supercritical water oxidation (SCWO), a method for
- 5 injecting a first fluid of a first temperature at a first flow rate into a second fluid of a second temperature at a second flow rate, said first fluid being corrosive only in a temperature range which excludes said second temperature and includes said first temperature or which lies between said first
- 10 and second temperatures, characterized by
- transporting the first fluid in a first conduit (107, 207) adapted therefore;
 - transporting the second fluid in a second conduit (103, 203) adapted therefore, wherein said first conduit (107, 207) ends in
 - 15 the interior of said second conduit (103, 203), and thus communicates with said second conduit; and
 - mixing the first and the second fluids (115, 215) in said second conduit within a mixing length downstream of said first conduit end, wherein said second conduit is provided with a tube
 - 20 or liner (105, 205) having at least its inner surface area made of a corrosion resistant material, and extending along said mixing length (115, 215) to protect said second conduit (103, 203) from corroding; wherein
 - the first and second temperatures and the first and second
 - 25 flow rates are selected such that a temperature of the mixed fluids downstream of said mixing length (115, 215) is obtained, at which said first fluid being substantially non-corrosive.

2. The method as claimed in Claim 1, wherein said first fluid is corrosive at said selected first temperature and wherein at least the inner surface area of said first conduit (107, 207) is made of a corrosion resistant material to protect said first conduit (107, 207) from corroding.
3. The method as claimed in Claim 1 or 2, wherein said first fluid contains nitric acid and said corrosive temperature range at which said first fluid is corrosive ranges between about 270°C and 380°C.
4. The method as claimed in any of Claims 1-3, wherein said first fluid contains sulfuric acid and/or hydrochloric acid and/or any halogen.
5. The method as claimed in any of Claims 1-4, wherein said second temperature is selected to be higher than said temperature range at which said first fluid is corrosive, and wherein the first and second temperatures and the first and second flow rates are selected such that said temperature of the mixed fluids downstream of said mixing length is higher than said temperature range at which said first fluid is corrosive.
6. The method as claimed in Claim 5, wherein said second fluid contains supercritical wastewater.
7. The method as claimed in Claim 6, wherein said second fluid contains nitrogenous compound.
8. The method as claimed in any of Claims 3-7, comprising feeding the mixed fluids in said second conduit (103, 203) to a reactor (18) of the high pressure and high temperature reaction system (10) for oxidation of waste material.

9. The method as claimed in any of Claims 3-7, wherein said second conduit (103, 203) is part of a reactor (18) of the high pressure and high temperature reaction system, wherein waste material is oxidized.
- 5 10. The method as claimed in any of Claims 1-4, wherein said second temperature is selected to be lower than said temperature range at which said first fluid is corrosive, and wherein the first and second temperatures and the first and second flow rates are selected such that said temperature of the mixed
10 fluids downstream of said mixing length is lower than said temperature range at which said first fluid is corrosive.
11. The method as claimed in Claim 10, wherein said second fluid contains cooling water.
12. The method as claimed in Claim 11, wherein said first fluid
15 contains destructured supercritical wastewater output from a reactor (18) of the high pressure and high temperature reaction system (10).
13. The method as claimed in Claim 12, wherein the mixed fluids in said second conduit (103, 203) are output from the high
20 pressure and high temperature reaction system (10).
14. The method as claimed in any of Claims 1-13, wherein said at least inner surface area of the tube or liner (105, 205) is made of a material selected from the group of titanium, zirconium, platinum, tantalum, niobium and alloys thereof.
- 25 15. A high pressure and high temperature reaction system suitable for oxidative waste treatment, particularly a reaction system for supercritical water oxidation (SCWO), characterized in

- a first conduit (107, 207) adapted to transport a first fluid of a first temperature at a first flow rate;
 - a second conduit (103, 203) adapted to transport a second fluid of a second temperature at a second flow rate, said first fluid being corrosive in a temperature range which excludes said second temperature and includes said first temperature or which lies between said first and second temperatures;
 - said first conduit (107, 207) ending inside said second conduit (103, 203), and thus communicates with said second conduit, such that the first and the second fluids can be mixed in said second conduit (103, 203) within a mixing length (115, 215) from the end of said first conduit and downstream such that a temperature of the mixed fluids downstream of said mixing length (115, 215) is obtained, at which said first fluid is substantially non-corrosive; and
 - a tube or liner (105, 205) with at least its inner surface area made of a corrosion resistant material, said tube or liner being located in, or constituting part of, said second conduit and extending along said mixing length (115, 215) to protect said second conduit from corroding, and, upstream and downstream of said tube or liner, said second conduit being made of a conventional construction material for high pressure and high temperature reaction systems suitable for supercritical water oxidation, such as a nickel based alloy.
16. The reaction system as claimed in Claim 15, wherein said first conduit is adapted to transport a first fluid, which is corrosive at said selected first temperature, and wherein at least the inner surface area of said first conduit (107, 207) is made of a corrosion resistant material to protect said first conduit (107, 207) from corroding.

17. The reaction system as claimed in Claim 15 or 16, wherein said first fluid contains nitric acid and said corrosive temperature range at which said first fluid is corrosive ranges between about 270°C and 380°C.
- 5 18. The reaction system as claimed in any of Claims 15-17, wherein said first fluid contains sulfuric acid and/or hydrochloric acid and/or any halogen.
- 10 19. The reaction system as claimed in any of Claims 15-18, wherein said second conduit is adapted to transport a second fluid at a second temperature, which is higher than said temperature range at which said first fluid is corrosive, and to transport the mixed fluids, said mixed fluids being of a temperature downstream of said mixing length, which is also higher than said temperature range at which said first fluid is
- 15 corrosive.
20. The reaction system as claimed in Claim 19, wherein said second fluid contains supercritical wastewater.
21. The reaction system as claimed in Claim 20, wherein said second fluid contains nitrogenous compound.
- 20 22. The reaction system as claimed in any of Claims 17-21, further comprising a reactor (18) for oxidation of waste material, wherein said second conduit is adapted to feeding the mixed fluids to said reactor.
- 25 23. The reaction system as claimed in any of Claims 17-21, comprising a reactor (18) for oxidation of waste material, wherein said second conduit (103, 203) is part of said reactor.
24. The reaction system as claimed in any of Claims 15-18, wherein said second conduit is adapted to transport a second

fluid at a second temperature, which is lower than said temperature range at which said first fluid is corrosive, and wherein said second conduit is adapted to transport the mixed fluids, said mixed fluids being of a temperature downstream of said mixing length, which is lower than said temperature range at which said first fluid is corrosive

25. The reaction system as claimed in Claim 24, wherein said second fluid contains cooling water.

26. The reaction system as claimed in Claim 25, comprising a reactor (18), wherein said first conduit is adapted to transport a first fluid, which contains destructured supercritical or subcritical wastewater output from said reactor.

27. The reaction system as claimed in Claim 13, comprising a high pressure and high temperature reaction system output, wherein said second conduit is adapted to transport said mixed fluids to said system output.

28. The reaction system as claimed in any of Claims 15-27, wherein said at least inner surface area of the tube or liner (105, 205) is made of a material selected from the group of titanium, zirconium, platinum, tantalum, niobium and alloys thereof.

29. The reaction system as claimed in any of Claims 15-28, wherein the tube or liner (105, 205) is removably arranged in said second conduit.

30. The reaction system as claimed in any of Claims 15-29, wherein said tube or liner (105, 205) is extending a predetermined distance (117, 217) upstream of said first conduit end.

31. The reaction system as claimed in any of Claims 15-30, wherein said second conduit is provided with means for holding and/or positioning the tube or liner (105, 205) in said second conduit (103, 203).

5 32. The reaction system as claimed in Claim 31, wherein said second conduit (103, 203) is provided with an elbow (119, 219) at the downstream end of the mixing length (115, 215) in order to prevent said tube or liner (105, 205) from moving along the inner surface of said second conduit (103, 203) in the
10 downstream direction.

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(54) Title: A HIGH PRESSURE AND HIGH TEMPERATURE REACTION SYSTEM

(57) Abstract: In a high pressure and high temperature reaction system suitable for oxidative waste treatment, particularly a reaction system for supercritical water oxidation (SCWO), a method is disclosed for injecting a first fluid of a first temperature at a first flow rate into a second fluid of a second temperature at a second flow rate, mixing the first and the second fluids within a mixing length (115, 215), and wherein the first and second temperatures and the first and second flow rates are selected such that a temperature of the mixed fluids downstream of said mixing length (115, 215) is obtained, at which said first fluid being substantially non-corrosive.

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A HIGH PRESSURE AND HIGH TEMPERATURE REACTION SYSTEM

TECHNICAL FIELD OF THE INVENTION

The present invention generally relates to an apparatus for mitigation of corrosion in a high pressure and high temperature reaction system, specifically in a system suitable for oxidative waste treatment under supercritical water conditions. The invention relates further to the reaction system itself and to a method in said reaction system.

DESCRIPTION OF RELATED ART AND BACKGROUND OF THE INVENTION

Several approaches for disposing of waste are available today, of which the major ones are landfilling and incineration. In recent years, another technique based on supercritical water oxidation (SCWO) has been commercialized, see, e.g. *Supercritical Water Oxidation Aims for Wastewater Cleanup*, C.M. Caruana, Chem. Eng. Prog., April 1995.

Supercritical water oxidation is a novel and advanced process for, inter alia, effective destruction of toxic substances, particularly organic pollutions, in wastewater and sludge. The process converts, fast and effectively, organic materials containing substantially carbon and hydrogen to carbon dioxide and water, at a temperature above the critical point of water (374°C and 22,13 MPa), while releasing energy. The process may be completely contained and the destruction efficiency is often higher than 99%.

Heavy metals present during the process are converted to their oxides whereas sulfur and phosphorous are converted to sulfate and phosphate, respectively. Halogens are converted to their corresponding acids, e.g., hydrochloric acid. Smaller amounts of nitrogen compounds, e.g. amines and ammonia, which exist in the

waste material flow, are converted to molecular nitrogen, and not to NO_x , which is an acidifying and fertilizing residual product and therefore undesirable in the effluent.

If, however, the waste material contains large amounts of ammonia and/or organic nitrogen compounds, substantial amounts of the nitrogen source may be found in the effluent as ammonia as a result of the destruction process. This phenomenon is undesirable as ammonia constitutes a fertilizing compound. Besides, discharge of ammonia without further purifying is very often imposed with restrictions.

It is known in the literature, e.g. through *Reactions of Nitrate Salts with Ammonia in Supercritical Water*, P.C. Dell'Orco et al., Ind. Eng. Chem., Vol. 36, No. 7, 1997, and references therein, that ammonia can be converted to molecular nitrogen during supercritical water oxidation conditions if nitric acid is used as a co-oxidant together with molecular oxygen, hydrogen peroxide or another suitable compound. The nitric acid has preferably to be supplied to the waste material flow firstly after that the organic contents have been destructed with oxygen as nitrate otherwise will compete with oxygen in the destruction of the organic contents. Furthermore, the nitric acid has to be dosed with high accuracy relative to the amount of ammonia (a stoichiometric amount is needed). If too little nitric acid is supplied, a remaining amount of ammonia will be left whereas too large amounts of nitric acid will result in an excess of nitrate in the effluent.

For purposes of strength and corrosion, nickel-based alloys, such as Hastelloy or Inconel, are employed for manufacturing of equipment for SCWO. Acids, and not at least nitric acid, are, however, in presence of oxygen strongly corrosive at high temperatures, though still subcritical ones, even if these corrosion resistant nickel alloys are used, see, e.g. *The Corrosion of Nickel-base Alloy 625 in Sub- and Supercritical*

Aqueous Solutions of HNO₃ in the Presence of Oxygen, P. Kritzer et al., J. Mater. Sci. Lett., 1999, in print, and references therein. It was found in the temperature-resolved corrosion measurements reported that the corrosion due to nitric acid was most severe at temperatures between about 270°C and 380°C, the same temperature range in which general corrosion is caused by the mixtures HCl/O₂ and H₂SO₄/O₂, respectively. At supercritical temperatures the corrosion rates were low.

For this reason, particular solutions must be employed for the entry of nitric acid into the supercritical wastewater flow containing ammonia or ammonium salts to avoid or at least minimize the corrosion.

However, as regards corrosion, generally the most troublesome compound in the supercritical water oxidation process is the chlorine element, since it is very common in various chemical substances. If the chlorine is present as an ion at elevated temperatures, it will corrode the construction materials mentioned above. The chlorine may have been an ion originally, liberated during heat up or in the reactor.

US 5,358,645 issued to Hong et al. disclose an apparatus and process for high temperature water oxidation, the apparatus (not in detail described) having a surface area, that may be exposed to corrosive material, composed of zirconia based ceramics. The ceramics may be employed as coatings or linings.

US 5,461,648 issued to Nauflett et al. disclose a supercritical water oxidation reactor with a corrosion-resistant lining. The inner surface of the reactor vessel is coated with artificial ceramic or diamond. A cylindrical baffle for introducing the oxygenating agent extends axially within the interior of the vessel and has its exterior surface inside the vessel coated with said artificial ceramic or diamond.

US 5,552,039 issued to McBrayer, Jr. et al. disclose a turbulent flow cold-wall reactor. It mentions, inter alia, that if the atmosphere in the reaction chamber is harsh and corrosive, the inside wall of the reaction chamber should preferably be made of
5 or covered with a coating or a liner withstanding the harsh atmosphere.

None of these US patents, is, however, discussing corrosion problems in terms of temperature dependent corrosivity, or the particular corrosion caused by the corrosive compounds discussed
10 above.

SUMMARY OF THE INVENTION

It is consequently an object of the present invention to provide an apparatus for use in a high pressure and high temperature reaction system, specifically in a system suitable for oxidative
15 waste treatment under supercritical water conditions, that mitigates or eliminates the occurrence of corrosion.

It is a further object of the invention to provide such an apparatus that is effective, robust, and easy to install and of low cost.

20 It is yet a further object of the invention to provide the apparatus in such a way that it is easily replaceable in the reaction system.

These objects among others are, according to one aspect of the invention, attained by an apparatus as claimed in Claim 1.

25 A further object of the present invention is to provide a method for disposing of waste using said apparatus.

Consequently, there is according to a second aspect of the present invention provided a method as claimed in Claim 22.

An advantage of the present invention is that it allows the main parts of the reaction system, including the reactor itself, to be constructed of a relatively inexpensive material such as nickel based and nickel-chromium alloys, and still use or be able to treat corrosive materials in the process.

BRIEF DESCRIPTION OF THE DRAWINGS

The present invention will become more fully understood from the detailed description of embodiments of the present invention given hereinbelow and the accompanying Figs. 1-3 which are given by way of illustration only, and thus are not limitative of the invention.

Fig. 1 shows a simplified block diagram of a reaction system suitable for oxidative waste treatment under supercritical water conditions wherein the present invention may be employed.

Fig. 2 shows, in cross-section, a first embodiment of an apparatus according to the present invention.

Fig. 3 shows, in cross-section, a second embodiment of an apparatus according to the present invention.

DETAILED DESCRIPTION OF EMBODIMENTS

In the following description, for purposes of explanation and not limitation, specific details are set fourth, such as particular hardware, applications, techniques, etc. in order to provide a thorough understanding of the present invention. However, it will be apparent to one skilled in the art that the present invention may be practiced in other embodiments that depart from these specific details. In other instances, detailed descriptions of well-known methods, protocols, apparatus, and circuits are omitted so as not to obscure the description of the present invention with unnecessary details.

Considering Fig. 1, the operation of a high pressure and high temperature reaction system 10 such as a system suitable for oxidative waste treatment under supercritical water conditions, will briefly be overviewed so that in the subsequent detailed description of the present invention, the operation of the inventive apparatus may be better understood.

A conventional reaction system 10 comprises a primary tank 12, a heat exchanger 14, a heater 16 and a reaction chamber 18. A primary wastewater stream 20 passes initially through the first compartment (not shown) of the heat exchanger 14, then through the heater 16, and enters the reaction chamber 18 under pressure, after it has been mixed with oxidant coming through feed line 22. The organic matter contained in the primary waste stream 20 is oxidized, and in sequence, the hot effluence passes through the second compartment (not shown) of the heat exchanger 14. As well known, heat exchangers usually have two compartments, physically isolated from each other, which, however, are heat-communicating. The second compartment transfers heat to the first compartment.

Constructing materials for the reactor and the tubing may comprise steel, nickel-based alloys, platinum, gold, titanium, zirconium, ceramics, ceramic composites and other corrosion resistant materials as the environment inside the reaction chamber and tubing may be hostile and corrosive. However, as many of the latter materials are highly expensive, an optimal compromise between cost, on one hand, and corrosion resistance, on the other hand, is to use nickel based alloys such as Hastelloy or Inconel, for the manufacturing of such equipment.

As already discussed in the prior art, there is a number of species that are very aggressive relative to these nickel based alloys within a finite temperature range, among them nitric acid, sulfuric acid and hydrochloric acid. All these three acids are strongly corrosive between about 270 and 380°C, but the

corrosion rates for the latter two acids are lower by a factor of ten than the one found for nitric acid, see said Kritzer article.

5 It is clear from the description above of the operation of the system that the wastewater flow, as well as any additives, will be heated from initial low temperatures, which probably are close to ambient temperatures, up to supercritical temperatures (above 374°C) for the oxidative treatment of the waste, whereafter the effluent is cooled either in a heat exchanger or
10 by mixing it with quench water or a combination of both.

The present inventors have realized that if the initial temperatures and the temperature of the cooled effluent are kept preferably well below 270°C and the temperature in the reaction chamber is kept preferably above 380°C, there is generally only
15 two sections of a reaction system made of nickel-based alloy that may be attacked by corrosive agents such as those mentioned above contained in, or supplied to, the wastewater flow, namely a "heating" section and a "cooling" section, where the temperatures are within the temperature interval of said
20 corrosion.

The present invention is thus concerned with such sections of the reaction system and how to design them in order to provide a reaction system of low cost and good corrosion resistance. The idea is to provide appropriate tubing (made of nickel based
25 alloy or other, preferably relatively inexpensive, material that is not corrosive resistant) of the system with a corrosive resistant tube or liner. The number of tubes or liners, their positions and their lengths are chosen in order to protect the system from corroding.

30 Hereinbelow will follow a few implementation examples of the present invention. Note that the terms "corrosive" and "corrosive-resistant material" as used in the description below

and in the appended claims should be understood as "corrosive" relative conventional construction material for high pressure and high temperature reaction systems suitable for supercritical water oxidation such as steel, nickel based alloys, nickel-chromium alloys and the like, at least within a given temperature interval, and "corrosive-resistant material" refers to unconventional expensive material which is corrosion-resistant relative a wide variety of harsh media such as acids, particularly the acids discussed above, halogens and the like, respectively. Examples of corrosion-resistant materials will be given below.

A first embodiment of the present invention, shown in Fig. 2, depicts an apparatus 101 for introducing nitric acid in a supercritical water flow containing ammonia or ammonium with the purpose of converting this to molecular nitrogen.

In a section of a reaction system tube 103, which preferably is the conduit between the heater 16 and the reaction chamber 18, or part of the reaction chamber itself, of Fig. 1, a separate tube or liner 105 of a corrosion resistant material is mounted, the outer surface of which is in fit with the inner surface of reaction system tube 103. Alternatively, tube 105 constitutes part of the reaction system tube 103 itself (not shown).

A feeding pipe 107 of relatively small diameter, is mounted through an opening of tube 103 and extends substantially axially with tube 103 and liner 105, and which ends in the interior of tube 103. Preferably, feeding pipe 107 and tube 103 are concentrically arranged for transportation of fluids, the former nitric acid and the latter preheated wastewater feed, in the same directions, as indicated by arrows 109-113. The temperature of the wastewater should preferably be above 380°C, and the temperature of the nitric acid should be low, preferably considerably lower than 270°C. Note that if the concentration of the corrosive agent is low, these temperature limits are not

very crucial, i.e., the corrosion would be low at temperatures slightly lower than 380°C and, particularly, at temperatures slightly higher than 270°C, e.g., 300°C.

5 By pumping nitric acid through the feeding pipe it will be preheated by the hot water flow and then get mixed with the supercritical water. The flow rates are such that the total flow (wastewater and nitric acid) becomes supercritical with a temperature of above 380°C after having reached a steady temperature state a certain distance 115 from the end of the feeding pipe, said distance being referred to as the heat transfer or mixing length. Accordingly, to avoid any risk of corrosion of the inner walls of tube 103, the length of the liner 105 should be of at least this length, and it should be localized to protect the inner walls of tube 103 within this 10 length. For practical reasons, the liner 105 may have an offset 117 in the end facing the end of the feeding pipe, i.e. extend beyond (upstream of) said feeding pipe end to avoid any risk of corrosion in that region. 15

The material of the liner and preferably of the feeding pipe is 20 chosen according to its corrosion resistance relative nitric acid at the occurring temperatures. Literature data shows that titanium, generally, is a suitable material, but also materials such as zirconium, platinum, tantalum, niobium and ceramics may be chosen. The entire liner, or an inner coating thereof, may be 25 constructed of such material.

Even if a limited degree of corrosion may exist using these materials, the components are relatively cheap and easy to replace when so needed.

30 Preferably, there are means for positioning and/or holding the liner in place. In the embodiment showed, tube 103 is provided with an elbow at the downstream end of the mixing length to prevent liner 105 from moving further downstream. However, any

suitable means for positioning and/or holding the liner, e.g. flanges at the inner walls of tube 103, may be used.

In experimental work, an injection apparatus as the one shown in Fig. 2, was used, the liner and the feeding pipe being made of titanium. The ammonia destruction was performed by pumping 65% nitric acid into the reaction system during several hours without any detected corrosion. When the liner and the feeding pipe were demounted and inspected no corrosion of these components was discovered. In contrast thereto, in an experiment in which nitric acid was pumped into a supercritical water flow containing ammonia through a T-pipe of Inconel 625, the pipe was destroyed through corrosion in just a few hours.

Consequently, by using an injection apparatus according to Fig. 2, nitric acid may safely be introduced without severe corrosion of the reaction system.

Furthermore, a substantial portion of the reaction between nitric acid and ammonia and/or ammonium will take part as early as in the section of the reaction system where the liner is localized, which further reduces the risk for severe corrosion.

Alternatively, feeding pipe 107 and tube 103 of Fig. 2 may be arranged for transportation of a wastewater feed containing a corrosive agent such as a halogen, and water or a wastewater feed in lack of such a corrosive agent, respectively. The water or wastewater in tube 103 is preferably at a supercritical temperature, whereas the corrosive wastewater may be cooler.

Referring next to Fig. 3, which illustrates an apparatus 201 according to a second embodiment of the present invention, a separate tube or liner 205 of a corrosion resistant material is mounted in a section of a reaction system tube 203, which is preferably at the effluent output or elsewhere in the exit path tubing. The outer surface of liner 205 is arranged to be in fit with the inner surface of the reaction system tube 203.

A first input tube 207, is mounted through an opening of tube 203 and extends substantially axially, preferably concentrically, with tube 203 and liner 205, and which ends in the interior of tube 203. A second input tube 208 is connected to tube 203 upstream from said end of input tube 207.

Input tube 207 and input tube 208 are arranged for transporting effluent from reactor 18 containing corrosive compounds such as nitric acid, sulfur acid, or the like, and quench water, respectively, in the directions as indicated by arrows 209-213. The effluent stream is supercritical or close to supercritical, and the temperature of the quench water is low, preferably at ambient temperature.

By pumping appropriate amounts of quench water through input tube 208, the effluent input through tube 207 will be cooled effectively by the quench water and get mixed with it. The flow rates are such that the total flow (effluent and quench water) will have a temperature of below a certain temperature, e.g. 270°C, depending on concentration of corrosive compounds, after having reached a steady temperature state a certain distance from the end of the input tube 207, said distance being referred to as the mixing length. Accordingly, to avoid any risk of corrosion of the inner walls of tube 203, the length of the liner 205 should be at least of this mixing length, and it should be localized to protect the inner walls of tube 203 within this length. For practical reasons, the liner 203 may have an offset in the end facing the end of tube 207, i.e. extend beyond (upstream of) said tube end, to avoid any risk of corrosion in that region.

The material of the liner and preferably of tube 207, as well as suitable means for positioning and/or holding the liner in place may be chosen as in the first embodiment.

The first and the second embodiments of the present invention may be modified to include a heat exchange for assisting in increasing or decreasing the temperature in tubes 103 and 203, respectively. Hereby, the lengths of liners 105 and 205, respectively, may be shortened.

As a further example of an implementation of the present invention (not illustrated in the drawings), an effluent from the reactor containing chlorine ions is pre-cooled in a heat exchanger by part of the incoming waste stream, to a temperature well above 380°C, e.g., 400°C. The effluent is then cooled by an apparatus according to the present invention to a sufficient low temperature, e.g., 260°C, to minimize corrosion. After leaving the apparatus, the effluent water mixture is further cooled by the remaining of the waste stream.

It will be obvious that the invention may be varied in a plurality of ways. For instance, the geometry and function of the reaction system and the appearance of the tubing may deviate substantially from the description above. Such and other variations are not to be regarded as a departure from the scope of the invention. All such modifications as would be obvious to one skilled in the art are intended to be included within the scope of the appended claims.

CLAIMS

1. In a high pressure and high temperature reaction system suitable for oxidative waste treatment, particularly a reaction system for supercritical water oxidation (SCWO), a method for
5 injecting a first fluid of a first temperature at a first flow rate into a second fluid of a second temperature at a second flow rate, said first fluid being corrosive only in a temperature range which excludes said second temperature and includes said first temperature or which lies between said first
10 and second temperatures, characterized by
- transporting the first fluid in a first conduit (107, 207) adapted therefore;
 - transporting the second fluid in a second conduit (103, 203) adapted therefore, wherein said first conduit (107, 207) ends in
15 the interior of said second conduit (103, 203), and thus communicates with said second conduit; and
 - mixing the first and the second fluids (115, 215) in said second conduit within a mixing length downstream of said first conduit end, wherein said second conduit is provided with a tube
20 or liner (105, 205) having at least its inner surface area made of a corrosion resistant material, and extending along said mixing length (115, 215) to protect said second conduit (103, 203) from corroding; wherein
 - the first and second temperatures and the first and second
25 flow rates are selected such that a temperature of the mixed fluids downstream of said mixing length (115, 215) is obtained, at which said first fluid being substantially non-corrosive.
2. The method as claimed in Claim 1, wherein said first fluid is corrosive at said selected first temperature and wherein at
30 least the inner surface area of said first conduit (107, 207) is

made of a corrosion resistant material to protect said first conduit (107, 207) from corroding.

3. The method as claimed in Claim 1 or 2, wherein said first fluid contains nitric acid and said corrosive temperature range at which said first fluid is corrosive ranges between about 270°C and 380°C.

4. The method as claimed in any of Claims 1-3, wherein said first fluid contains sulfuric acid and/or hydrochloric acid and/or any halogen.

5. The method as claimed in any of Claims 1-4, wherein said second temperature is selected to be higher than said temperature range at which said first fluid is corrosive, and wherein the first and second temperatures and the first and second flow rates are selected such that said temperature of the mixed fluids downstream of said mixing length is higher than said temperature range at which said first fluid is corrosive.

6. The method as claimed in Claim 5, wherein said second fluid contains supercritical wastewater.

7. The method as claimed in Claim 6, wherein said second fluid contains nitrogenous compound.

8. The method as claimed in any of Claims 3-7, comprising feeding the mixed fluids in said second conduit (103, 203) to a reactor (18) of the high pressure and high temperature reaction system (10) for oxidation of waste material.

9. The method as claimed in any of Claims 3-7, wherein said second conduit (103, 203) is part of a reactor (18) of the high pressure and high temperature reaction system, wherein waste material is oxidized.

10. The method as claimed in any of Claims 1-4, wherein said second temperature is selected to be lower than said temperature

range at which said first fluid is corrosive, and wherein the first and second temperatures and the first and second flow rates are selected such that said temperature of the mixed fluids downstream of said mixing length is lower than said temperature range at which said first fluid is corrosive.

11. The method as claimed in Claim 10, wherein said second fluid contains cooling water.

12. The method as claimed in Claim 11, wherein said first fluid contains destructed supercritical wastewater output from a reactor (18) of the high pressure and high temperature reaction system (10).

13. The method as claimed in Claim 12, wherein the mixed fluids in said second conduit (103, 203) are output from the high pressure and high temperature reaction system (10).

14. The method as claimed in any of Claims 1-13, wherein said at least inner surface area of the tube or liner (105, 205) is made of a material selected from the group of titanium, zirconium, platinum, tantalum, niobium and alloys thereof.

15. A high pressure and high temperature reaction system suitable for oxidative waste treatment, particularly a reaction system for supercritical water oxidation (SCWO), characterized in

- a first conduit (107, 207) adapted to transport a first fluid of a first temperature at a first flow rate;

- a second conduit (103, 203) adapted to transport a second fluid of a second temperature at a second flow rate, said first fluid being corrosive in a temperature range which excludes said second temperature and includes said first temperature or which lies between said first and second temperatures; wherein

- said first conduit (107, 207) ends in the interior of said second conduit (103, 203), and thus communicates with said second conduit, such that the first and the second fluids can be mixed in said second conduit (103, 203) within a mixing length (115, 215) downstream of said first conduit end in such manner that a temperature of the mixed fluids downstream of said mixing length (115, 215) is obtained, at which said first fluid is substantially non-corrosive; and

- a tube or liner (105, 205) with at least its inner surface area made of a corrosion resistant material, said tube or liner being located in, or constituting part of, said second conduit and extending along said mixing length (115, 215) to protect said second conduit from corroding.

16. The reaction system as claimed in Claim 15, wherein said first conduit is adapted to transport a first fluid, which is corrosive at said selected first temperature, and wherein at least the inner surface area of said first conduit (107, 207) is made of a corrosion resistant material to protect said first conduit (107, 207) from corroding.

17. The reaction system as claimed in Claim 15 or 16, wherein said first fluid contains nitric acid and said corrosive temperature range at which said first fluid is corrosive ranges between about 270°C and 380°C.

18. The reaction system as claimed in any of Claims 15-17, wherein said first fluid contains sulfuric acid and/or hydrochloric acid and/or any halogen.

19. The reaction system as claimed in any of Claims 15-18, wherein said second conduit is adapted to transport a second fluid at a second temperature, which is higher than said temperature range at which said first fluid is corrosive, and to transport the mixed fluids, said mixed fluids being of a temperature downstream of said mixing length, which is also

higher than said temperature range at which said first fluid is corrosive.

20. The reaction system as claimed in Claim 19, wherein said second fluid contains supercritical wastewater.

5 21. The reaction system as claimed in Claim 20, wherein said second fluid contains nitrogenous compound.

22. The reaction system as claimed in any of Claims 17-21, further comprising a reactor (18) for oxidation of waste material, wherein said second conduit is adapted to feeding the
10 mixed fluids to said reactor.

23. The reaction system as claimed in any of Claims 17-21, comprising a reactor (18) for oxidation of waste material, wherein said second conduit (103, 203) is part of said reactor.

24. The reaction system as claimed in any of Claims 15-18, wherein said second conduit is adapted to transport a second
15 fluid at a second temperature, which is lower than said temperature range at which said first fluid is corrosive, and wherein said second conduit is adapted to transport the mixed fluids, said mixed fluids being of a temperature downstream of
20 said mixing length, which is lower than said temperature range at which said first fluid is corrosive.

25. The reaction system as claimed in Claim 24, wherein said second fluid contains cooling water.

26. The reaction system as claimed in Claim 25, comprising a
25 reactor (18), wherein said first conduit is adapted to transport a first fluid, which contains destructed supercritical or subcritical wastewater output from said reactor.

27. The reaction system as claimed in Claim 13, comprising a high pressure and high temperature reaction system output,

wherein said second conduit is adapted to transport said mixed fluids to said system output.

28. The reaction system as claimed in any of Claims 15-27, wherein said at least inner surface area of the tube or liner (105, 205) is made of a material selected from the group of titanium, zirconium, platinum, tantalum, niobium and alloys thereof.

29. The reaction system as claimed in any of Claims 15-28, wherein the tube or liner (105, 205) is removably arranged in said second conduit.

30. The reaction system as claimed in any of Claims 15-29, wherein said tube or liner (105, 205) is extending a predetermined distance (117, 217) upstream of said first conduit end.

31. The reaction system as claimed in any of Claims 15-30, wherein said second conduit is provided with means for holding and/or positioning the tube or liner (105, 205) in said second conduit (103, 203).

32. The reaction system as claimed in Claim 31, wherein said second conduit (103, 203) is provided with an elbow (119, 219) at the downstream end of the mixing length (115, 215) in order to prevent said tube or liner (105, 205) from moving along the inner surface of said second conduit (103, 203) in the downstream direction.

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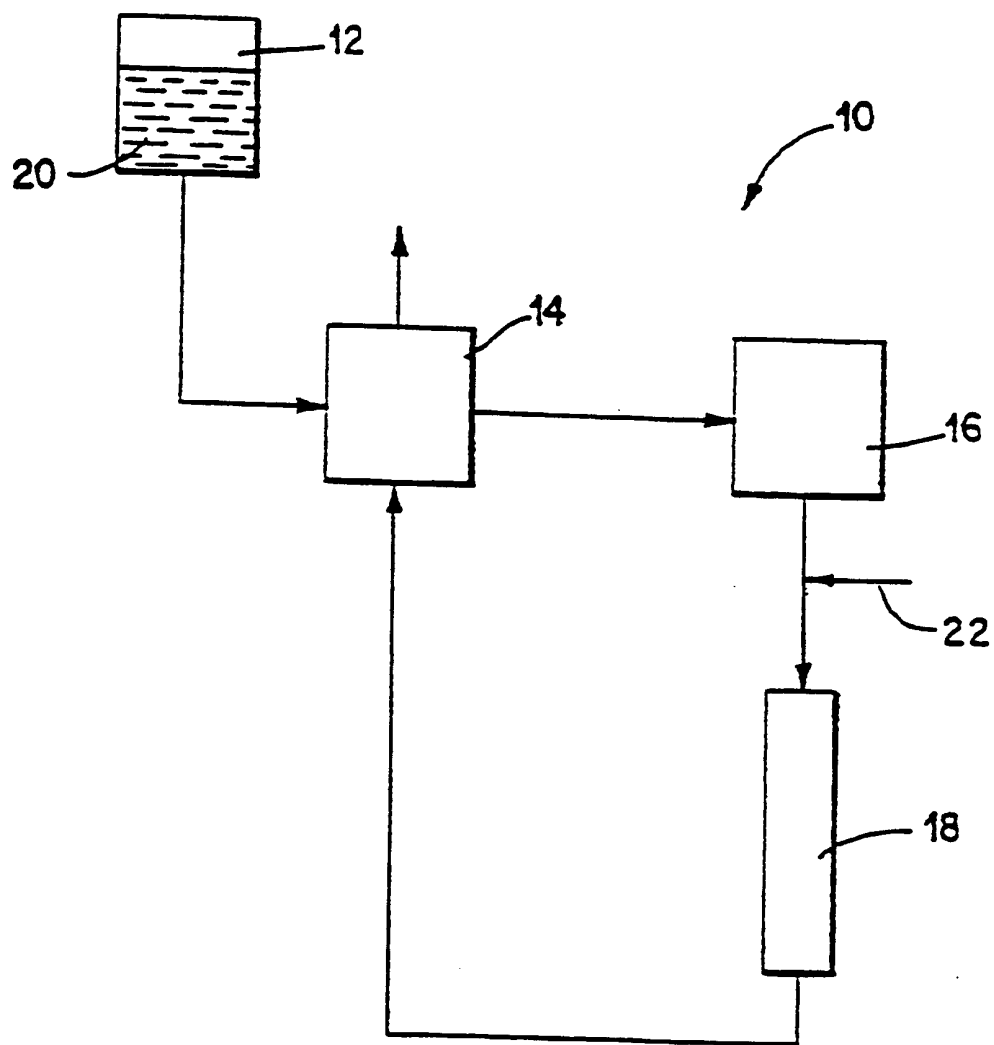


Fig. 1

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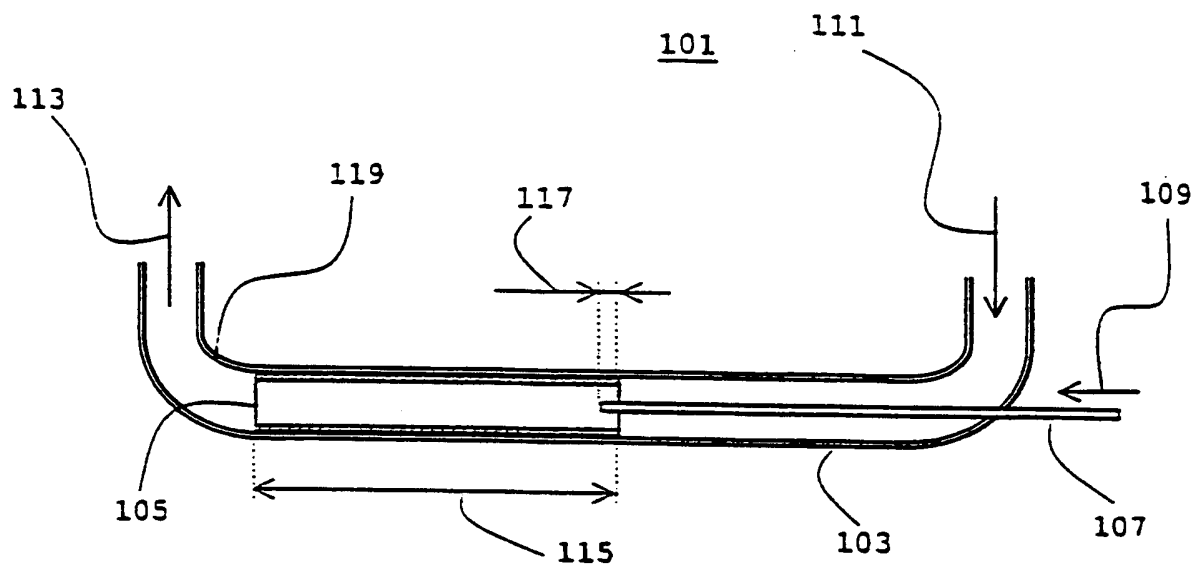


Fig. 2

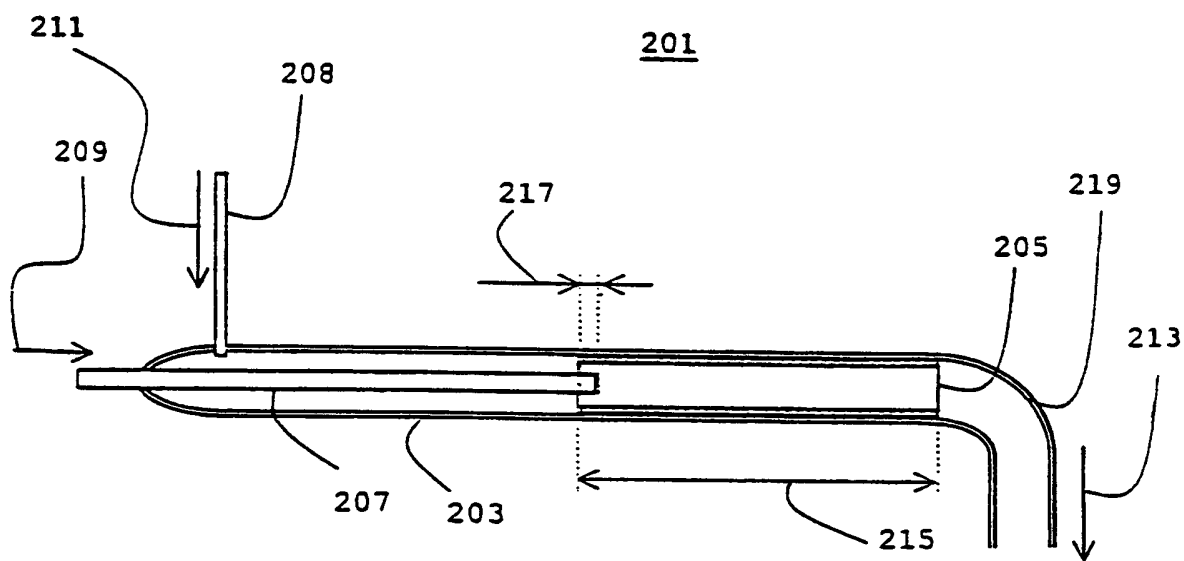


Fig. 3

INTERNATIONAL SEARCH REPORT

International application No.

PCT/SE 00/01675

A. CLASSIFICATION OF SUBJECT MATTER

IPC7: C02F 1/72, B01J 3/04, B01J 19/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC7: C02F, B01J, F16L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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P,A	WO 0002820 A1 (L'ELECTROLYSE ET AL), 20 January 2000 (20.01.00), page 28, line 29 - page 29, line 6, claims 1,27-28 --	1-32

☒ Further documents are listed in the continuation of Box C.
 ☒ See patent family annex.

* Special categories of cited documents	"I" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E" earlier application or patent but published on or after the international filing date	"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&" document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search 9 January 2001	Date of mailing of the international search report 11-01-2001
Name and mailing address of the ISA/ Swedish Patent Office Box 5055, S-102 42 STOCKHOLM Facsimile No. +46 8 666 02 86	Authorized officer Mårten Hulthén/ELY Telephone No. +46 8 782 25 00

INTERNATIONAL SEARCH REPORT

International application No.

PCT/SE 00/01675

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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